UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF CHEMICAL SAFETY
AND POLLUTION PREVENTION

May 21, 2015

MEMORANDUM:

SUBJECT: Review of MRID 49141001 "Release of silver from textiles", HeiQ Study Number HQE-A-005.

PC Code: 072599	DP Barcode: 414798
Decision No.: 482767	Registration No.: 85249-1
Petition No.: NA	Regulatory Action: Conditional Registration Follow-up
Risk Assess Type: NA	Case No.: NA
TXR No.: NA	CAS No.: NA
MRID No.: 49141001	40 CFR: NA

FROM: Timothy Dole, CIH, Industrial Hygienist
Risk Assessment and Science Support Branch
Antimicrobials Division (7510P)

THRU: Timothy Leighton, Senior Scientist
Steve Weiss, Chief
Risk Assessment and Science Support Branch
Antimicrobials Division (7510P)

TO: Seiichi Murasaki, Chemical Review Manager
Regulatory Management Branch I
Antimicrobials Division (7510P)

1.0 Introduction

This study was submitted by HeiQ Materials AG in support of the textile use for their product AGS-20. This product is registered for use as a preservative in synthetic textiles such as polyester and in natural synthetic blends such as cotton/polyester. It is applied as a surface treatment to previously manufactured textiles or as incorporated treatment during textile manufacture. The application rate in the final treated article is 20 mg silver /kg textile (i.e. 20 ppm) for surface applications and 100 mg silver/kg (100 ppm) for incorporation applications. The study consisted of a washing machine test where fabric samples were washed in a simulated washer according to the ISO test method for colorfastness. [redacted]

2.0 Materials Tested

[redacted]

3.0 Testing Methods

The test method was modeled after the ISO 105-C06 test method "Colour fastness to domestic and commercial laundering" that was used in Geranio et al. (2009) and Lorenz et al. (2012). The ISO test method uses steel balls in a simulated washing machine. The ISO method was used in this study with some modifications as follows:

[redacted]

Claimed confidential by the data submitter

4.0 Sample Preparation Methods

5.0 Sample Analysis

6.0 Quality Control

[redacted]

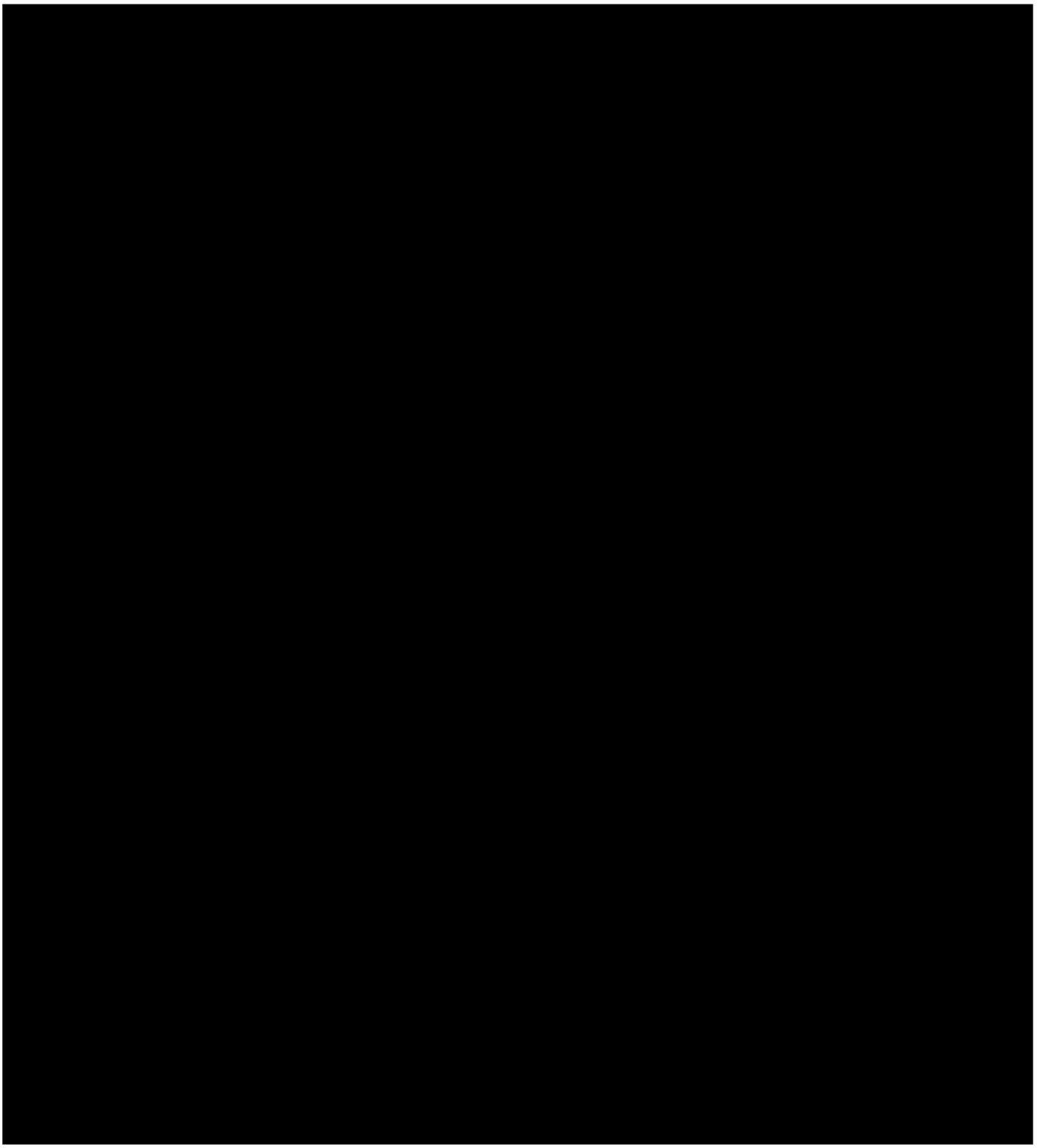
Claimed confidential by the data submitter

7.0 Chemical Analysis Results

[redacted]

8.0 Electron Microscopy Results

Claimed confidential by the data submitter



9.0 Study Limitations

[redacted]

10.0 EPA Comparison to Other Studies

There have been two nanosilver leaching studies published since the completion of the HeiQ study. One study measured the release of silver from nanotechnology based consumer products (Quadros, 2013) and the other study measured the dermal exposure to textiles that contain silver nanoparticles (Stefaniak, 2014).

Quadros, 2013 – Release of Silver from Nanotechnology Based Consumer Products

This study measured the release of silver from a variety of consumer products including a plush toy (interior foam and exterior fur) and a baby blanket by soaking the test articles in tap water, simulated saliva, sweat or urine for two hours. In addition, the articles soaked in saliva were subjected to simulated chewing using a bead beater.

The leachate was filtered using a 0.45 micron filter and the amount of silver was quantified using ICP-MS. If silver was detected in the leachate, the leachate was analyzed a second time after being filtered using a 3-KDa filtering unit. The amount of silver leached from the plush toy foam was 0.5 $\pm$ 0.0, 3.7 + 0.1, 38.3 = 2.4 and 36.1 + 1.6 percent when using tap water, saliva, sweat, and urine respectively. The amount of silver leached from the plush toy fur was 5.6 $\pm$ 0.2 percent using saliva and 2.6 $\pm$ 0.6 percent using sweat. The amount of silver leached from the baby blanket ranged from 1.1 $\pm$ 0.1 percent to 4.4 $\pm$ 0.3 percent depending upon which medium (tap water, saliva, sweat, urine, HCL or saline) was tested.

Almost all of the silver released was thought to be in the ionic form. The average ionic fraction of silver released from the plush toy foam and baby blanker into saliva, sweat and urine plush was 87.1 $\pm$ 2 percent. Because previous testing of the 3-KDa filtering unit indicated that it retained ionic silver, the actual ionic fraction was inferred to be higher than the measured ionic fraction.

Stefaniak, 2014 – Dermal Exposure Potential from Textiles that Contain Silver Nanoparticles

This study measured the release of silver from two products: HVAC™ Gloves and Silvermax underwear. The HVAC gloves contained 88 % polyester/12% lycra and the silver was incorporated in the masterbatch. The SilverMax™ underwear contained 96% polyester interwoven with 4% X-Static silver coated fibers.

The study used artificial biological fluids including a simple human sweat (pH 5.8, temp = 36^{O} C, a simple human saliva (pH 6.8, temp = 37^{O} C) and a skin surface film liquid (SSFL) model fluid. The SSFL was formulated at two pHs (4.5 and 5.3),with two types of sebum (with or without vitamin E) and

was maintained at two temperatures (36^{O} and 45^{O} C). Silver transfer from the textile to skin was measured in a barrier migration test where sebum coated paper filters wetted with simulated sweat solution were placed on top of electron microscopy grids which were placed on top of the textile samples. Silver release was measured in an aggressive extraction test where the textile sample was immersed in biological fluid and rotated end over end at 60 rpm in a temperature controlled incubator for thirty minutes. Silver release was also measured in simulated use test were the textile was wetted in SSFL buffered to pH 5.3 for three consecutive days, laundered in detergent and bleach and wetted for three more days. The laundering was simulated by stirring each textile swatch in 25 ml of 40^{O} C wash water for 15 minutes, followed by a 5 minute rest and stirred for an additional 15 minutes.

In the transfer test, no silver was detected using ICP-AES and no particles were observed on the TEM grid samples, thus it was concluded that silver did not migrate from the textiles to the filters. In the aggressive extraction test, the mass dissolved ranged from 0.01 to 0.11 percent depending on the fluid type, sebum type, pH and temperature. The particles on the filters that were used to filter the fluids after the aggressive extraction were characterized using FE-SEM-EDX. Silver containing particles were only observed for the samples from SilverMax textile exposed to the SSFL at pH 4.5. These particles had a hydrodynamic diameter (D_H) of 164 ± 14 nm at 36^{O} C and 165 ± 55 nm at 45^{O} C and may reflect both silver/chlorine particles and salt crystals in the fluid. In the simulated use test the total amount of silver released by the end of the test protocol was 0.51 ± 0.4 percent for the SilverMax textile and 0.21 percent $\pm$ 0.01 for the HVAC gloves. The amount of silver released in particulate form was 0.29% of the total mass of silver in the SilverMax textile samples but almost no silver particulate was released from the HVAC textile.

11.0 Summary and Conclusions

Summary

[redacted]

Conclusions

[redacted]

As discussed in the literature (Akaighe, 2011, Muarer, 2012 and Yin, 2012) nanoparticle creation has been observed in natural water containing humic acid or dissolved organic matter and exposed to sunlight; however, the conditions under which these studies were conducted (neutral pH and sunlight) are somewhat different than the conditions of the HEIQ study [redacted].

There have been two nanosilver leaching studies published since the completion of the HeiQ study. One study measured the release of silver from nanotechnology based consumer products (Quadros, 2013) and the other study measured the dermal exposure to textiles that contain silver nanoparticles (Stefaniak, 2014). The leaching rates measured in these studies was very either low (i.e. less than 1 percent) or consisted mainly of silver ions, which supports the results reported in the HeiQ study.

[redacted]

References

Akaighe et al., 2011. Humic Acid-Induced Silver Nanoparticle Formation under Environmentally Relevant Conditions, Environmental Science and Technology, 2011, 45, pp 3895-3901.

Geranio et al., 2009. The Behavior of Silver Nanoparticles during Washing. Geranio, L., Heuberger, M., Nowack, B., *Environmental Science and Technology* 43:8113-8118, September, 2009.

Lorenz, C., Windler, L., von Goetz, N. et al. 2012. Characterization of silver release from commercially available functional (nano) textiles. *Chemosphere* 89:817-824.

Muarer et al., 2012 Reduction and Reoxidation of Humic Acid: Influence on Speciation of Cadmium and Silver. Environmental Science and Technology, 2012, 46, pp 8808-8816.

Quadros and Marr, 2011. Silver Nanoparticles and Total Aerosols Emitted by Nanotechnology-Related Consumer Spray Products. Environmental Science and Technology, 2011, 45, pp 10713-10719.

Stefaniak et al, 2014. Dermal Exposure Potential from Textiles that Contain Silver Nanoparticles, International Journal of Occupational and Environmental Health, Volume 20, Number 3, pp 220-234, 2014.

US EPA, 2000. Assigning Values to Nondetected/Non-Quantified Pesticide Residues in Human Health Food Exposure Assessments, Office of Pesticide Programs, U.S Environmental Protection Agency, March 23, 2000

Yin, 2012. Sunlight-Induced Reduction of Ionic Ag and Au to Metallic Nanoparticles by Dissolved Organic Matter. ACS Nano 6, 7910-7919.